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### (54) BLEACHING AGENTS

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(56) References cited:

<b>EP-A- 0 103 416</b>	<b>EP-A- 0 349 220</b>
<b>EP-A- 0 373 691</b>	<b>EP-A- 0 376 360</b>
<b>DE-A- 3 906 768</b>	<b>GB-A- 2 129 457</b>

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**Description**Field of the invention.

5 This invention is concerned with organic peroxyacids and their manufacture. The invention is particularly concerned with the stability of said organic peroxyacids.

Background of the invention.

10 It is well known that organic peroxyacids are able to function as bleaching agents in a detergent composition. Organic peroxyacids which have been proposed for such use include peroxybenzoic acid, peroxyphthalic acid, isomers and substituted derivatives thereof, peroxyalkanoic acids and diperoxyalkanedioic acids such as diperoxyazelaic acid and diperoxydodecanedioic acid. Discussion of such acids can be found in US Patents 4,100,095, 4,170,453 and 4,325,828 as well as numerous other documents. Another series of acids which have been proposed are phthalimido substituted peroxyalkanoic acids disclosed in EP-A-325288. Amidoperoxyacids which contain a polar amide linkage  
15 part way along a hydrocarbon chain have been disclosed in US Patents 4,634,551 and 4,686,063.

An obstacle to the commercial utilization of organic peroxyacids is various problems of stability. US Patent 4,170,453 recognises and discusses separate categories of instability problem. One is instability of the peroxyacid when subjected to heat (or to friction or shock which give rise to local heating), another is storage stability of the peroxyacid prior to use and a third problem concerns stability of a peroxyacid-containing wash liquor. It is well known that peroxyacids are inherently unstable and capable of undergoing an exothermic decomposition if heated or, in many instances, if handled in such a way that heat is generated by application of force, e.g. as a result of friction or impact. This form of instability is more pronounced for compounds with higher proportions of available oxygen. WO 90/07501 (Interox) describes the variation in stability of peroxyacids according to features of their structure. This document teaches that phthalimido peroxyacetic acid is somewhat explosive whereas longer chain homologues are relatively more stable.  
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Storage stability has been presented in the prior art as a somewhat different problem. Of course, a material which undergoes abrupt exothermic decomposition is not displaying stability in storage but even without such decomposition a peroxyacid may undergo progressive decomposition during storage as a result of reaction with impurities or other materials with which it has been mixed.  
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It has been recognised that transition metal ions can catalyse unwanted decomposition of peroxyacid compounds and it has, therefore, been proposed to mix peroxyacid compounds with chelating agents to enhance storage stability of organic peroxyacid-containing compositions and/or stabilise the wash liquor against unwanted decomposition of the peroxyacid. Inter-alia such use of chelating agents is disclosed in US Patents 4,170,453 and 4,100,095. This disclosure is also reviewed in EP-349220.  
35

In contrast with such problems of storage stability, the prior art has treated the exothermic decomposition of peroxyacids initiated by heat as unavoidable. Thus US Patent 4,100,095 explains that there is a temperature called the self-accelerating decomposition temperature, at which the exothermic decomposition of organic peroxyacid can become a runaway reaction leading to the generation of sufficient heat to cause ignition. It is pointed out that such decomposition can be initiated by point sources of heat such as friction.  
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In order to control this hazard it is taught that the peroxyacid should be mixed with a so-called exotherm control agent which undergoes an endothermic decomposition when heated. Consequently in the event of some local heating of the composition, the heat liberated by decomposition of the peroxyacid is taken up by endothermic decomposition of the exotherm control agent and runaway decomposition is prevented.  
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Following on from these teachings, EP-A-0 373 691 discloses the use of fully neutralised carboxylated polymers, such as polyacrylates, as exotherm control agents for reducing the tendency of peroxycarboxylic acids to undergo exothermic decomposition such as may lead to detonation or explosion.

Consistent with these understandings, the prior art has disclosed that organic peroxyacids may be incorporated into compositions which contain only a minority proportion of peroxyacid and which also contain a chelating agent for sequestering transition metal ions, this chelating agent being incorporated for the purpose of promoting storage stability of the peroxyacid and/or stability of the peroxyacid in a wash liquor during use. Examples of such compositions are disclosed in US Patents 4,091,544 and 4,170,453.  
50

European published application EP-A-0 349 220 is concerned with amidoperoxyacids which contain an amide link in a hydrocarbon chain. This reference teaches that the storage stability of these peracids can be improved considerably by washing the peracids with phosphate buffer and leaving some phosphate in contact with the peracid after washing. It is pointed out that the amidoperoxyacids are acid sensitive and this beneficial effect of phosphate buffer is principally attributed to neutralisation of residual strong acid left from the reaction in which the amido peroxyacid is prepared. The phosphates which are used may be orthophosphates or pyrophosphates or a mixture of the two. Such phosphates  
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have the ability to sequester transition metal ions. However, in this prior document they are relied upon for buffering ability and it is suggested that additional chelating agents may be incorporated to further promote storage stability.

Thus the teaching of the prior art is that storage stability of organic peroxyacids and compositions containing them can be promoted by measures which include the incorporation of chelating agents. However, no measures are proposed to counteract the exothermic instability initiated by heat or pressure apart from the incorporation of a so-called exotherm control agent to prevent local thermal decomposition from becoming a runaway reaction.

#### Definition of the invention

In radical contrast with this established view, we have found that the thermal instability of peroxyacids made by conventional methods can be beneficially modified. Broadly, we have found that by contacting a peroxyacid with a binding agent for transition metal ions it is possible to raise the temperature at which thermal decomposition occurs.

Accordingly in a first aspect the present invention provides the use of a binding agent for transition metal ions, excluding fully neutralized polyacrylates, for enhancing stability of a substantially water-insoluble organic peroxyacid against exothermic decomposition initiated by heat.

In a second aspect this invention provides a composition consisting essentially of 80 to 99.9% by weight of a substantially water-insoluble organic peroxyacid mixed with from 0.1 to 20% by weight of a binding agent for transition metal ions, which binding agent and peroxyacid are stable in the presence of each other, with the proviso that the peroxyacid does not include any amide linkage.

The improvement in stability when the organic peroxyacid is in contact with the binding agent for transition metal ions can be observed by differential scanning calorimetry (DSC) which shows the temperature or temperature range over which exothermic decomposition occurs. In general, bringing the organic peroxyacid into contact with the binding agent in accordance with this invention leads to a composition in which the temperature of thermal decomposition has increased. The decomposition may also occur over a temperature range of different width. Thus, differential scanning calorimetry may show an increase in the temperature at which maximum decomposition occurs and/or an increase in the temperature at which decomposition begins. The outcome of a DSC measurement will show these results as a shift in the position of a peak, or as a shift in the base of the peak at its lower temperature side, respectively.

Bringing the organic peroxyacid into contact with the binding agent for transition metal ions can be done in various ways.

One possibility is simply dry-mixing the two materials in solid form to obtain a mixture containing from 80 to 99.9% by weight of the peroxyacid.

Another possibility is to wash the substantially water-insoluble peroxyacid with a solution or suspension of the binding agent and leave from 0.3 to 3% by weight, preferably from 1 to 2% by weight, more preferably from 1 to 1.5% by weight, of the binding agent, as calculated on the total weight of peroxyacid and binding agent, in contact with the peroxyacid. The final pH of the thus obtained material is in the range of from 3.5-6.0, more preferably of from 4-5.

Thus a third aspect of this invention provides a process for enhancing the thermal stability of a substantially water-insoluble organic peroxyacid which does not include any amide linkage, comprising washing the peroxyacid with an aqueous solution or suspension of a binding agent for transition metal ions under conditions such that from 0.3 to 3% by weight of the binding agent, as calculated on the total weight of binding agent and peroxyacid, remains in contact with the peroxyacid and a final pH of from 3.5-6.0 is obtained.

A preferred possibility is to precipitate the organic peroxyacid in the presence of the binding agent, such that 0.3-3% by weight, preferably 1-2% by weight, more preferably 1-1.5% by weight of the binding agent, as calculated on the total weight of peroxyacid and binding agent, remains in contact with the peroxy acid. The final pH of the thus-obtained material is in the range of from 3.5-6, preferably from 4-5. This leads to a beneficial enhancement of stability, and moreover it is then possible to wash the peroxyacid further without losing the enhanced stability. Thus, a composition obtained in this way is more robust than compositions obtained in other ways.

Therefore, a fourth aspect of this invention provides a process for enhancing the stability of a substantially water-insoluble organic peroxyacid which comprises precipitating the peroxyacid in the presence of a binding agent for transition metal ions such that 0.3 - 3.0% by weight of the binding agent, as calculated on the total weight of binding agent and peroxyacid, remains in contact with the peroxyacid and a final pH of from 3.5 - 6.0 is obtained.

This preferred process can be carried out as a step in the conventional procedure by which a peroxyacid is made. This procedure consists of oxidising the appropriate carboxylic acid with hydrogen peroxide in a strong acid medium, and then quenching the reaction. Conventionally this quenching has been done by running the reaction mixture into ice and water. In order to implement the preferred process of the invention the reaction mixture is run into an aqueous solution containing a precursor for the binding agent.

Another, possible way to implement this invention is to dissolve the peroxyacid in an organic solvent, (dichloromethane for instance) and wash the solution with an aqueous solution of the binding agent before separating

the peroxyacid from the organic solvent. A suitable aqueous solution of binding agent would be phosphate buffer at about pH 4.

Yet another to use the binding agent to enhance the stability of the organic peroxyacid is to bring the binding agent into contact with an organic acid and then use the resulting acid as the starting material for making the corresponding peroxyacid.

Thus a process for enhancing the stability of the organic peroxyacid may comprise either

(i) washing the corresponding acid with an aqueous solution of the binding agent for transition metal ions under conditions that 0.3-3% by weight of the binding agent remains in contact with the acid, or

(ii) precipitating the corresponding acid in the presence of a said binding agent for transition metal ions, and then (iii) oxidising the acid from step (i) or step (ii) to the peroxyacid.

As a result of the above-indicated processes of the invention, a particulate composition is effectively obtained, said composition comprising particles of the organic peroxyacid with the binding agent trapped in said particles.

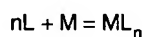
#### The binding agent

Suitable binding agents should not react to any substantial extent with the peroxyacid, under conditions to which they are exposed. Thus for example, ethylene diamine tetraacetic acid is oxidised by peroxyacids in solution and so would not be suitable, except for use by mixing with dry solid peroxyacid.

The binding agent may possibly form an insoluble salt with at least one transition metal or may function by forming a co-ordination complex with at least one transition metal ion. Thirdly the binding agent may bind to transition metal sites in impurity particles present in colloidal suspension.

It is generally desirable that a binding agent should have good affinity for one or more transition metal ions, e.g. for ferric ion which is a likely trace contaminant.

The affinity of a complexing agent L for a metal ion M can be expressed by the equilibrium constant for the complex forming reaction



The equilibrium constant K is given by

$$K = \frac{[ML_n]}{[L]^n[M]}$$

where  $[ML_n]$ ,  $[L]$  and  $[M]$  are the concentrations of the co-ordination complex, the free complexing agent and the free metal ion in aqueous solution under specified conditions of temperature and ionic strength, e.g. 25°C and zero ionic strength.

Such an equilibrium constant is also referred to as the stability constant for the complex. It may be the overall equilibrium constant for the formation of a complex through several steps in sequence, or the equilibrium constant for a single step reaction.

For this invention, a binding agent which forms a co-ordination complex should preferably form a complex with at least one transition metal ion with a stability constant K of at least  $10^6$  in aqueous solution at 25°C and at zero ionic strength.

Numerous stability constants are recorded in the scientific literature. Two compilations of such data are:

Stability Constants of Metal Ion Complex, IUPAC Chemical Data Series No. 21, and

Critical Stability Constants by Arthur E Martell and Robert M Smith.

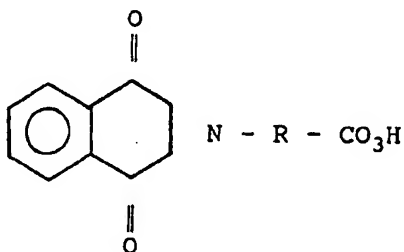
Preferably a complexing agent forms such a co-ordination complex with at least one transition metal ion, significant examples of which are the ions of iron, manganese, cobalt, nickel, zinc and copper. More preferably the complexing agent forms such a complex with at least  $Fe^{3+}$ .

Binding agents for transition metals which are suitable for the process aspects of present invention include dihydrogen orthophosphate, pyrophosphate, polyacrylate (but in the use aspects of the invention fully neutralised polyacrylates are excluded), titanium chloride, stannic salts, and stannous salts. The effectiveness and hence the suitability of a binding agent can be assessed by differential scanning calorimetry as mentioned further below. The preferred binding agent is dihydrogen orthophosphate.

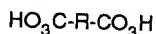
The peroxyacid

The present invention is applicable to substantially water-insoluble organic peroxyacids, having a solubility between 0.1 and 5 mmol in water at ambient temperatures and a pH of from 3.5-6. As indicated above, a wide variety of such acids are known.

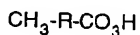
Peroxyacids which are particularly envisaged include phthalimido-substituted peroxyalkanoic acids of formula



where R is an arylene or alkylene group of up to 10 carbon atoms, notably alkylene of 2 to 7 carbon atoms. Other categories of peroxyacids are the diperoxy alkane dioic acids of formula



and peroxyalkanoic acids of formula



wherein, in either case, R denotes an alkylene group of 2 to 18 carbon atoms especially 2 to 12 carbon atoms, optionally incorporating a heteroatom in the carbon chain, such as the nitrogen atom of an amide linkage.

Another category is the corresponding aromatic acids in which R denotes an arylene group, e.g. perbenzoic acid, substituted perbenzoic acid and diperoxyisophthalic acid.

The production of peroxyacids may be carried out by known methods. Preferred is the oxidation of the corresponding organic acid using hydrogen peroxide in an acid medium, notably an organic sulphonic acid such as methanesulphonic acid or a mineral acid such as sulphuric acid.

When the reaction medium comprises a mineral acid, such as sulphuric acid, all or part of it can be premixed with the hydrogen peroxide to form an equilibrium mixture containing for example permonosulphuric acid that can itself perform the peroxidation reaction. Such premixing separates the exothermic dilution/reaction between hydrogen peroxide and sulphuric acid from the peroxidation reaction.

The stability of a sample of a peroxycarboxylic acid can be assessed by differential scanning calorimetry (DSC). In this technique a sample is heated steadily and the heat input rate is monitored. An endothermic transition, such as melting, appears as a peak in the heat input rate at the melting temperature. Exothermic decomposition appears as a drop in heat input. The results are normally shown by means of a recording pen which draws a graph of heat input against temperature.

EXAMPLES

The invention will be explained and demonstrated further by the following Examples which refer to the drawings. All of the drawing figures reproduce the print-out from a differential scanning calorimeter and are thus a graph of heat input rate against temperature for a sample of material.

Example 1

A phosphate buffer solution was prepared by dissolving 14 grams analytical grade sodium dihydrogen orthophosphate in 1 litre of deionised water. The acidity of the buffer solution was measured and found to be pH 4.5.

A commercial sample of diperoxydodecanedioic acid, determined by analysis to be substantially pure, was investigated by DSC. The resulting print-out is reproduced as Fig. 1. As can be seen the material showed a strong exothermic

decomposition at approximately 83°C.

1 gram of this peroxyacid was mixed with 20 ml of the phosphate buffer solution and stirred at 60°C for 1 hour. After this the water-insoluble acid was filtered off and dried in air at 20°C. It was then again investigated by DSC and the resulting print-out is reproduced as Fig. 2. As can be seen from this figure there was a remarkable change. The sample displayed an endothermic transition between 90 and 100°C, attributed to melting and the exothermic decomposition took place at temperatures in excess of 100°C.

#### Examples 2.1-2.4

The thermal stability of several other types of peroxyacids was investigated using the same test method as used in Example 1. By applying DSC measurements, exothermic decomposition temperatures could be found for these peroxyacids before and after washing them with the phosphate buffer solution. The results are shown in Table 1

TABLE 1

Example no.	Type of peroxyacid	Exotherm.decomposition temperatures (°C)	
		before wash	after wash
2.1	Pernonanoic acid	55	125
2.2	Perbenzoic acid	102	114
2.3	p-sulphonated perbenzoic acid	199	220
2.4	m-chloro-perbenzoic acid	91	110

It can be seen that in all above cases a significant increase of the decomposition temperature occurred after washing with the phosphate buffer solution.

#### Example 3

Phthalimido-6-peroxyhexanoic acid was prepared by a method similar to Example 1 in WO 90/07501 but with the procedure for working up the reaction modified to embody the present invention, as follows:

Phthalimido-6-hexanoic acid (2g) was added to stirred methanesulphonic acid (15mls = 22.29) in a beaker, forming a solution therein. The mixture was cooled to below 5°C in a water/ice bath. 85% by weight aqueous hydrogen peroxide (approx 80% w/w) was added with continuous stirring into the reaction mixture progressively during a period of about 5 to 10 minutes while keeping the temperature below 5°C, until a total amount of 3.5 moles per mole of carboxylic acid has been introduced, i.e. a 2.5 molar excess compared with the stoichiometric amount. The reaction mixture was then stirred for a further 50 minutes.

At the end of this time the reaction mixture was poured into a stirred, ice cold solution consisting of 30 grams disodium hydrogen orthophosphate dissolved in 750 grams demineralised water. Before addition this solution was at approximately pH 8.0 and at the end of the addition the pH had dropped to between pH 4.0 and pH 4.5.

The desired peroxyacid precipitated from the solution and was washed with an aqueous solution containing 13g/l  $\text{NaH}_2\text{PO}_4$ , pH 4.5, and collected by filtration. The filter cake was allowed to dry in air and examined by DSC. The resulting print-out is reproduced as Fig. 3. This showed endothermic melting at about 90°C followed by exothermic decomposition reaching a peak at approximately 165°C.

Some of the peroxyacid prepared in this way was washed with demineralised water before drying and DSC. The print-out from that DSC is reproduced as Fig. 4. This showed very little change from the acid which had not been washed with water. This indicates that when the peroxyacid is precipitated in the presence of a binding agent for transition metals, the stabilisation effect is not dependent on binding agent which is merely adsorbed at the surface of the particles of the acid.

#### Example 4

A commercial sample of phthalimido-6-peroxyhexanoic acid was investigated by DSC. The resulting print-out is reproduced as Fig. 5. This sample contained about 5% of the corresponding phthalimido hexanoic acid. It can be seen that this sample showed endothermic melting between about 80 and 90°C followed by exothermic decomposition reaching a maximum at about 125°C.

A sample of this peroxyacid was purified to approximately 98% purity by dissolving 5g of the peroxyacid in 150ml dichloromethane, then washing the solution with two 50ml quantities of aqueous  $\text{Na}_2\text{HPO}_4$  buffer solution at pH 8.5, then washing with water and drying over sodium sulphate. After this the peroxyacid was recovered by evaporating the

organic solvent. Thus purified acid was again investigated by DSC. The print-out is reproduced as Fig. 6 which shows rapid decomposition sharply following the onset of melting at about 90°C. Recrystallization from acetonitrile produced a purer peroxyacid which was even less stable.

5 A 1 gram sample of the commercial peroxyacid was washed with 20ml phosphate buffer at pH 4.5 in the same manner as in Example 1. After drying the phosphate-washed acid it was investigated by DSC.

The resulting print-out resembled Fig. 3. It again showed endothermic melting at about 90°C followed by exothermic decomposition. This reached a peak at approximately 155°C, which was slightly lower than in Fig. 3.

10 When a sample of the peroxyacid was washed with phosphate buffer as just described and then washed again with demineralised water and dried the resulting acid was much less stable, decomposing exothermically at approximately 90°C. This indicates that the stabilisation is brought about by orthophosphate which has remained mixed with the peroxyacid, presumably adsorbed on the surface of peroxyacid particles.

#### Example 5

15 Phthalimido-6-peroxyhexanoic acid purified as in Example 3 was mixed, dry, with sodium dihydrogen phosphate in an acid:phosphate weight ratio of 8:2. The resulting mixture was then examined by DSC and the trace is reproduced as Fig. 7. Comparison with Fig. 6 shows that the sharp exothermic decomposition peak shown in Fig. 6 has been transformed into a broader peak extending from approximately 100 to 160°C with a maximum at about 140°C.

#### Example 6

20 The previous Example was repeated using polyacrylic acid in place of sodium dihydrogen phosphate. The resulting DSC trace is reproduced as Fig. 8. Once again the exothermic decomposition has been transformed from the sharp peak below 100° seen in Fig. 6 into a broad band extending over a temperature range.

#### **Claims**

- 30 1. Use of a binding agent for transition metal ions, excluding fully neutralized polyacrylates, for enhancing stability of a substantially water-insoluble organic peroxyacid against exothermic decomposition initiated by heat.
2. Use according to claim 1, which is by dry-mixing the binding agent with the peroxyacid in solid form to obtain a mixture containing 80-99.9% by weight of the peroxyacid.
- 35 3. Use according to claim 1, which is by washing the peroxyacid with an aqueous solution or suspension of the binding agent for transition metal ions under conditions such that from 0.3 to 3% by weight of the binding agent, as calculated on the total weight of peroxyacid and binding agent, remains in contact with the peroxyacid and a final pH of the thus treated peroxyacid of from 3.5-6.0 is obtained.
- 40 4. Use according to claim 1, which is by precipitating the peroxyacid in the presence of the binding agent for transition metal ions such that 0.3-3% by weight of the binding agent, as calculated on the total weight of peroxyacid and binding agent, remains in contact with the peroxyacid and a final pH of the thus precipitated peroxyacid of from 3.5-6.0 is obtained.
- 45 5. Use according to claim 4, wherein the peroxyacid is made by oxidation of a corresponding carboxylic acid, in the presence of a strong acid, selected from sulphuric acid and sulphonic acid, and then the reaction mixture is mixed with an aqueous solution containing a precursor for the binding agent.
- 50 6. Use according to claim 1, which is by contacting a carboxylic acid with the binding agent, and then oxidising the carboxylic acid to the corresponding peroxyacid.
7. A process for enhancing the stability against exothermic decomposition initiated by heat of a substantially water-insoluble organic peroxyacid which does not include any amide linkage, comprising washing the peroxyacid with an aqueous solution or suspension of a binding agent for transition metal ions under conditions such that from 0.3 to 3% by weight of the binding agent, as calculated on the total weight of binding agent and peroxyacid, remains in contact with the peroxyacid and a final pH of the thus treated peroxyacid of from 3.5-6.0 is obtained.
- 55 8. A process for enhancing the stability against exothermic decomposition initiated by heat of a substantially water-



insoluble organic peroxyacid, which comprises precipitating the peroxyacid in the presence of a binding agent for transition metal ions such that 0.3-3.0% by weight of the binding agent, As calculated on the total weight of binding agent and peroxyacid, remains in contact with the peroxyacid and a final pH of the thus precipitated peroxyacid of from 3.5-6.0 is obtained.

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9. A process for enhancing the stability against exothermic decomposition initiated by heat of a substantially water-insoluble organic peroxyacid, which comprises dry-mixing the peroxyacid with a binding agent for transition metal ions such that a composition containing 80-99.9% by weight of the peroxyacid is obtained.

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10. A composition consisting essentially of 80-99.9% by weight of a substantially water-insoluble organic peroxyacid, which acid does not include any amide linkage, mixed with 0.1-20% by weight of a binding agent for transition metal ions, which binding agent and acid are stable in the presence of each other.

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11. A composition according to claim 10, comprising particles of the organic peroxyacid with the binding agent for transition metal ions trapped in the particles of peroxyacid.

#### Patentansprüche

20

1. Verwendung eines Bindemittels für Übergangsmetallionen, mit Ausnahme von vollständig neutralisierten Polyacrylaten, zur Verbesserung der Stabilität einer im wesentlichen wasserunlöslichen organischen Peroxysäure gegenüber einer durch Wärme initiierten exothermen Zersetzung.

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2. Verwendung nach Anspruch 1, die durch Trockenvermischen des Bindemittels mit der Peroxysäure in fester Form erfolgt, wobei ein Gemisch erhalten wird, das 80 bis 99,9 Gew.-% der Peroxysäure enthält.

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3. Verwendung nach Anspruch 1, die durch Waschen der Peroxysäure mit einer wäßrigen Lösung oder Suspension des Bindemittels für Übergangsmetallionen unter derartigen Bedingungen erfolgt, daß 0,3 bis 3 Gew.-% des Bindemittels, bezogen auf das Gesamtgewicht aus Peroxysäure und Bindemittel, in Kontakt mit der Peroxysäure verbleiben und ein End-pH-Wert der so behandelten Peroxysäure von 3,5 bis 6,0 erreicht wird.

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4. Verwendung nach Anspruch 1, die durch Fällern der Peroxysäure in Anwesenheit des Bindemittels für Übergangsmetallionen in einer derartigen Weise erfolgt, daß 0,3 bis 3 Gew.-% des Bindemittels, bezogen auf das Gesamtgewicht aus Peroxysäure und Bindemittel, in Kontakt mit der Peroxysäure verbleiben und ein End-pH-Wert der so gefällten Peroxysäure von 3,5 bis 6,0 erreicht wird.

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5. Verwendung nach Anspruch 4, wobei die Peroxysäure durch Oxidieren einer entsprechenden Carbonsäure in Gegenwart einer starken Säure, die aus Schwefelsäure und Sulfonsäure ausgewählt ist, hergestellt wird und das Reaktionsgemisch anschließend mit einer einen Vorläufer für das Bindemittel enthaltenden wäßrigen Lösung vermischt wird.

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6. Verwendung nach Anspruch 1, die durch Inberührungbringen einer Carbonsäure mit dem Bindemittel und anschließendes Oxidieren der Carbonsäure zu der entsprechenden Peroxysäure erfolgt.

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7. Verfahren zur Verbesserung der Stabilität einer im wesentlichen wasserunlöslichen organischen Peroxysäure, die keinerlei Amidbindung enthält, gegenüber einer durch Wärme initiierten exothermen Zersetzung durch Waschen der Peroxysäure mit einer wäßrigen Lösung oder Suspension eines Bindemittels für Übergangsmetallionen unter derartigen Bedingungen, daß 0,3 bis 3 Gew.-% des Bindemittels, bezogen auf das Gesamtgewicht aus Bindemittel und Peroxysäure, in Kontakt mit der Peroxysäure verbleiben und ein End-pH-Wert der so behandelten Peroxysäure von 3,5 bis 6,0 erreicht wird.

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8. Verfahren zur Verbesserung der Stabilität einer im wesentlichen wasserunlöslichen organischen Peroxysäure gegenüber einer durch Wärme initiierten exothermen Zersetzung durch Fällern der Peroxysäure in Gegenwart eines Bindemittels für Übergangsmetallionen in einer derartigen Weise, daß 0,3 bis 3 Gew.-% des Bindemittels, bezogen auf das Gesamtgewicht aus Bindemittel und Peroxysäure, in Kontakt mit der Peroxysäure verbleiben und ein End-pH-Wert der so gefällten Peroxysäure von 3,5 bis 6,0 erreicht wird.

9. Verfahren zur Verbesserung der Stabilität einer im wesentlichen wasserunlöslichen organischen Peroxysäure ge-

genüber einer durch Wärme initiierten exothermen Zersetzung durch Trockenvermischen der Peroxysäure mit einem Bindemittel für Übergangsmetallionen in einer derartigen Weise, daß eine 80 bis 99,9 Gew.-% Peroxysäure enthaltende Zusammensetzung erhalten wird.

- 5 10. Zusammensetzung aus im wesentlichen 80 bis 99,9 Gew.-% einer im wesentlichen wasserunlöslichen organischen Peroxysäure, die keinerlei Amidbindungen enthält, im Gemisch mit 0,1 bis 20 Gew.-% eines Bindemittels für Übergangsmetallionen, wobei das Bindemittel und die Säure in Gegenwart des jeweiligen anderen Partners stabil sind.
- 10 11. Zusammensetzung nach Anspruch 10, die Teilchen der organischen Peroxysäure mit dem in den Peroxysäureteilchen eingeschlossenen Bindemittel für Übergangsmetallionen umfaßt.

#### Revendications

- 15 1. Utilisation d'un agent liant pour les ions métalliques de transition, à l'exclusion de polyacrylates complètement neutralisés, destinée à renforcer la stabilité d'un peroxyacide organique substantiellement insoluble dans l'eau face à la décomposition exothermique initiée par la chaleur.
- 20 2. Utilisation selon la Revendication 1, par mélange à sec de l'agent liant avec le peroxyacide sous forme solide afin d'obtenir un mélange comportant 80 à 99,9 % en masse du peroxyacide.
- 25 3. Utilisation selon la Revendication 1, en lavant le peroxyacide avec une solution ou une suspension aqueuse de l'agent liant pour les ions métalliques de transition dans des conditions telles qu'entre 0,3 et 3 % en masse de l'agent liant, calculé sur la masse totale du peroxyacide et de l'agent liant, demeure en contact avec le peroxyacide, et qu'un pH final compris entre 3,5 et 6,0 du peroxyacide ainsi traité est obtenu.
- 30 4. Utilisation selon la Revendication 1, en faisant précipiter le peroxyacide en présence de l'agent liant pour les ions métalliques de transition de sorte qu'entre 0,3 à 3 % en masse de l'agent liant, calculé sur la masse totale du peroxyacide et de l'agent liant, demeure en contact avec le peroxyacide, et qu'un pH final compris entre 3,5 et 6,0 du peroxyacide ainsi précipité est obtenu.
- 35 5. Utilisation selon la Revendication 4, dans laquelle le peroxyacide est fabriqué par oxydation d'un acide carboxylique correspondant, en présence d'un acide fort, sélectionné à partir d'acide sulfurique et d'acide sulfonique, suite à quoi le mélange de réaction est mélangé avec une solution aqueuse comportant un précurseur pour l'agent liant.
- 40 6. Utilisation selon la Revendication 1, en mettant en contact un acide carboxylique avec l'agent liant, puis en oxydant l'acide carboxylique avec le peroxyacide correspondant.
- 45 7. Un procédé destiné à renforcer la stabilité face à la décomposition exothermique initiée par la chaleur, d'un peroxyacide organique substantiellement insoluble dans l'eau qui ne comprend aucune liaison d'amide, comprenant l'étape consistant à laver le peroxyacide avec une solution ou une suspension aqueuse d'un agent liant pour les ions métalliques de transition dans des conditions telles qu'entre 0,3 à 3 % en masse de l'agent liant, calculé sur la masse totale du peroxyacide et de l'agent liant, demeure en contact avec le peroxyacide, et qu'un pH final compris entre 3,5 et 6,0 du peroxyacide ainsi traité est obtenu.
- 50 8. Un procédé destiné à renforcer la stabilité face à la décomposition exothermique initiée par la chaleur, d'un peroxyacide organique substantiellement insoluble dans l'eau, comprenant l'étape consistant à faire précipiter le peroxyacide en présence d'un agent liant pour les ions métalliques de transition de sorte qu'entre 0,3 à 3,0 % en masse de l'agent liant, calculé sur la masse totale du peroxyacide et de l'agent liant, demeure en contact avec le peroxyacide, et qu'un pH final compris entre 3,5 et 6,0 du peroxyacide ainsi précipité est obtenu.
- 55 9. Un procédé destiné à renforcer la stabilité face à la décomposition exothermique initiée par la chaleur, d'un peroxyacide organique substantiellement insoluble dans l'eau, comprenant l'étape consistant à mélanger à sec le peroxyacide avec un agent liant pour les ions métalliques de transition de sorte qu'une composition comportant 80 à 99,9 % en masse du peroxyacide est obtenue.
10. Une composition composée essentiellement de 80 à 99,9 % en masse d'un peroxyacide organique substantiellement insoluble dans l'eau et ne comprenant aucune liaison d'amide, mélangé avec 0,1 à 20 % en masse d'un

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agent liant pour les ions métalliques de transition, lesquels agent liant et acide sont stables en présence l'un de l'autre.

- 5 11. Une composition selon la Revendication 10, comportant des particules du peroxyacide organique avec l'agent liant pour les ions métalliques de transition emprisonnées dans les particules de peroxyacide.

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Fig.1

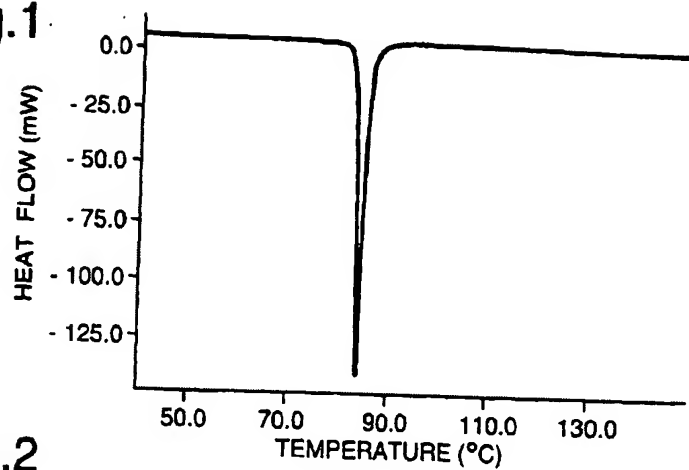


Fig.2

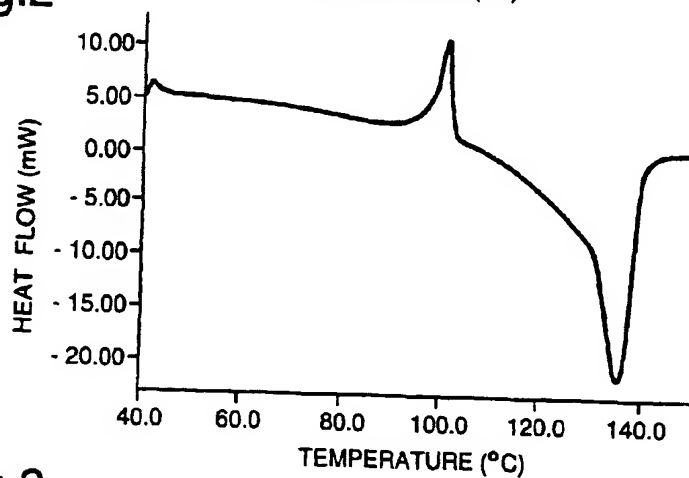


Fig.3

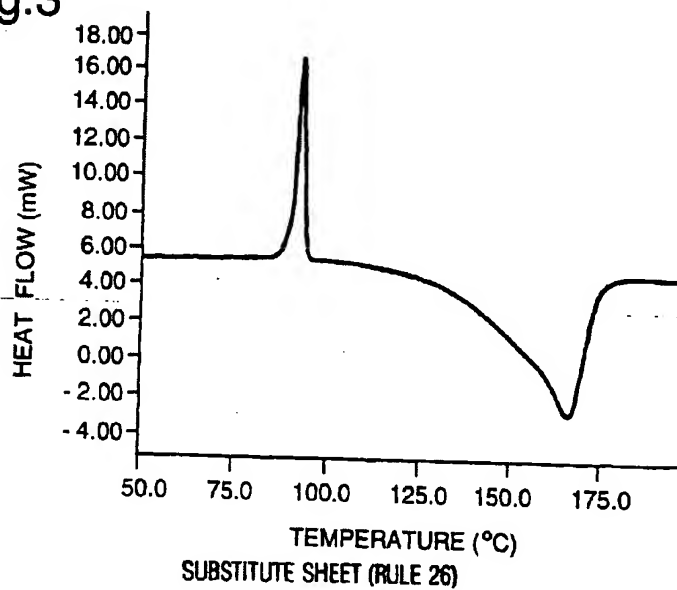


Fig.4

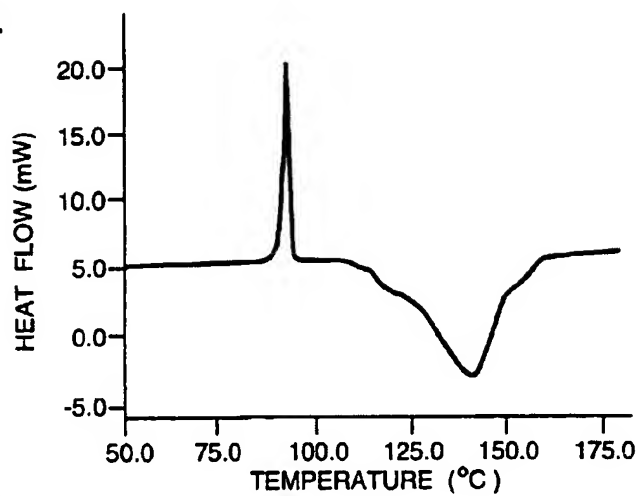


Fig.5

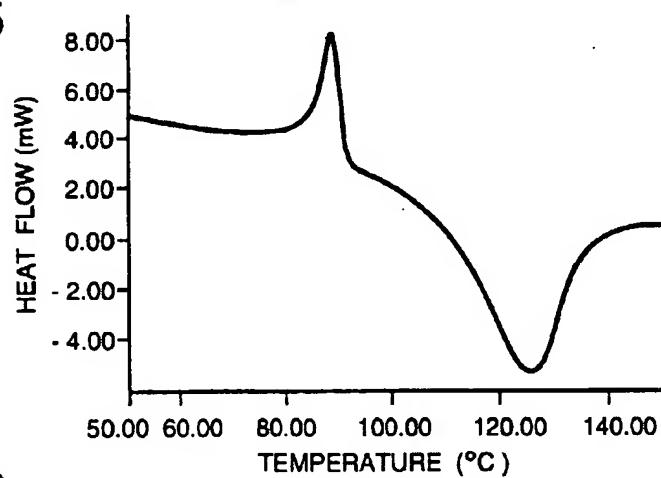


Fig.6

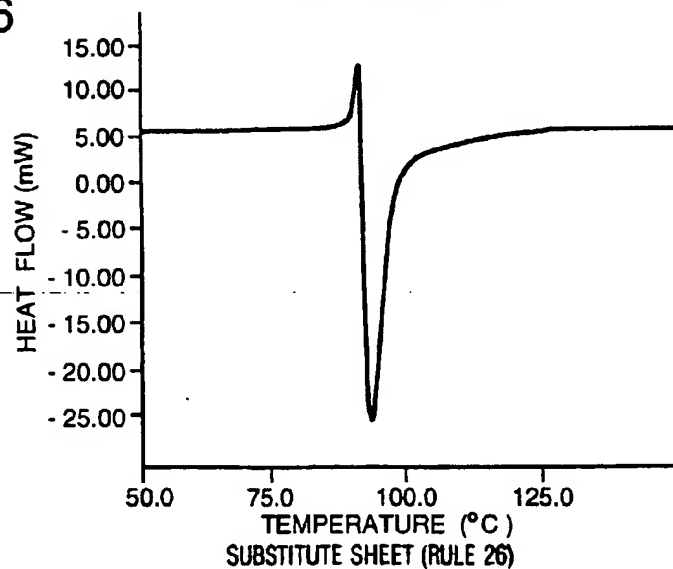


Fig.7

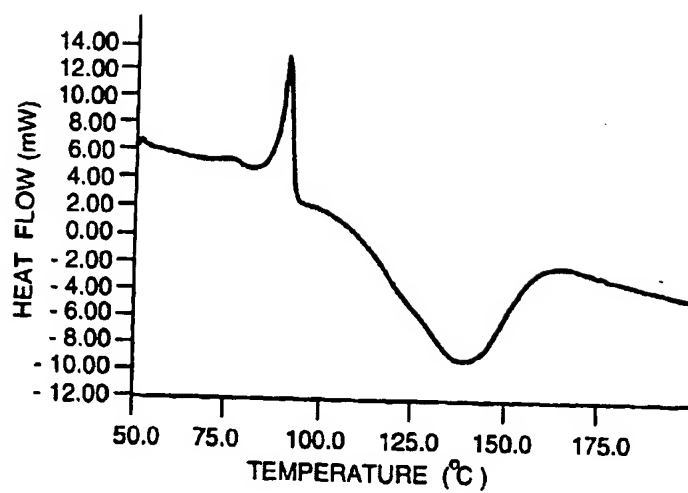


Fig.8

